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Jun Chen
University of Wollongong, junc@uow.edu.au

Gordon G. Wallace
University of Wollongong, gwallace@uow.edu.au

Jiaxing Lu
University of Wollongong

Aijian Zhang
University of Wollongong

Weimin Zhang
University of Wollongong, weimin@uow.edu.au

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Abstract

In the quest for catalysts for the electrocatalytic reduction of , a cobalt phthalocyanine/polypyrrole (CoPc/PPy) composite electrode has been developed. The electrode is prepared by drop casting CoPc onto the PPy film from the CoPc/tetrahydrofuran solution (1 mg/mL). The onset potential for reduction occurred at potentials 160 mV more positive than observed with a simple PPy electrode. Furthermore, in the potentiostatic electrolysis, the catalytic current for reduction at CoPc/PPy was very stable, with a higher current density and current efficiency when compared to the PPy electrode.

Keywords

Electrocatalytic, reduction, carbon, dioxide, cobalt, phthalocyanine, incorporated, polypyrrole

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Electrocatalytic Reduction of Carbon Dioxide by Cobalt-Phthalocyanine-Incorporated Polypyrrole

Aijian Zhang,[a,b] Weimin Zhang,[a] Jiaxing Lu,[b] Gordon G. Wallace,[a,*] and Jun Chen[a,*,z]

[a]*Australian Research Council Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, New South Wales 2522, Australia*
[b]*Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University, Shanghai 200062, China*

In the quest for catalysts for the electrocatalytic reduction of CO_2, a cobalt phthalocyanine/polypyrrole (CoPc/PPy) composite electrode has been developed. The electrode is prepared by drop casting CoPc onto the PPy film from the CoPc/tetrahydrofuran solution (1 mg/mL). The onset potential for CO_2 reduction occurred at potentials 160 mV more positive than observed with a simple PPy electrode. Furthermore, in the potentiostatic electrolysis, the catalytic current for CO_2 reduction at CoPc/PPy was very stable, with a higher current density and current efficiency when compared to the PPy electrode.
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The advent of global warming, associated with increasing atmospheric carbon dioxide (CO_2) concentrations, has stimulated research into the utilization of CO_2. The transformation of CO_2 to organic substances is a promising long-term objective. For the past decade, methods of reducing CO_2 to CO, formaldehyde, formate, methanol, methane, or oxalate, using electrochemical methods which consume less energy than traditional chemical reduction processes and can proceed at a moderate temperature and atmospheric pressure, have been developed.[1-5]

The direct electrochemical reduction of CO_2 on various metal electrodes requires large overpotentials (more negative than −2 V vs saturated calomel electrode).[6-10] It is therefore important to search for active electrocatalysts which can mediate electrochemical reduction of CO_2 at lower potentials. Numerous transition-metal (mainly Co and Ni) complexes, such as macrocyclic cobalt or nickel, cobalt phthalocyanine (CoPc), or porphyrin, have been reported to have such catalytic effects.[11-13] The use of these catalysts, however, has generally been limited by their degradation during electrolysis. It is thus necessary to investigate the electrochemical reduction of CO_2 at a modified electrode, on which the complex is more stable. Both Lieber and Lewis[14] and Meshitsuka et al.[15] reported the electroreduction of CO_2 at a CoPc-modified graphite electrode in citrate buffer and obtained CO as the main product. The electrochemical reduction of CO_2 at cobalt-octabutoxyphthalocyanine-coated graphite electrodes was investigated by Abe et al.[16] The reduction of CO_2 at a cobalt(II) tetraphenylporphyrin-pyridine-modified glassy carbon (GC) electrode showed a high catalytic activity for CO_2 reduction to CO.[17]

In recent years, the combination of polymer and metal complex catalysts has provided an alternative route to the electrochemical reduction of CO_2. The reduction of CO_2 at Prussian blue/polymer/metal complex-based electrodes in the aqueous solution[18-21] was investigated. CO_2 was reduced at −0.8 V (vs Ag/AgCl) and the reaction products were formic acid, lactic acid, acetic acid, methanol, and ethanol. The electrocatalytic conversion of CO_2 on polypyrrole (PPy)- or polyaniline-modified electrodes under high pressure in methanol resulted in the formation of CH_3COOH as the main product.[22-24]

In this article, we present the study of electrocatalytic CO_2 reduction at the CoPc/PPy-modified GC electrode in the 0.1 M $LiClO_4$/ACN–H_2O solution. The CoPc/PPy composite electrode was then investigated via a potentiostatic method and showed the enhanced electrocatalytic activity and stability for CO_2 reduction.

* Electrochemical Society Active Member.
z E-mail: junc@uow.edu.au

Experimental

Reagents.— Pyrrole was purchased from Sigma and was always redistilled before use. CoPc was from Strem Chemicals, while $LiClO_4$, acetonitrile (ACN), and tetrahydrofuran (THF) were commercial chemicals from Ajax Finechem and used as received.

Preparation of CoPc/PPy-modified GC electrode.— The electrochemical polymerization of the PPy film was carried out by cyclic voltammetry (CV) at the GC electrode cycled between −0.2 and 0.9 V (Ag/Ag^+) with a scan rate of 50 mV/s in the ACN solution containing 0.1 M $LiClO_4$ and 0.1 M pyrrole. The resultant electrode was washed carefully with ACN to remove the impurities adsorbed on the PPy film and dried in air at room temperature. Then, 4 μL of the CoPc/THF solution (1 mg/mL) was directly cast onto the PPy film and dried in air. These resulting PPy electrodes with/without CoPc modification were investigated for further characterization and catalytic testing for CO_2 reduction.

Characterizations.— The PPy and CoPc/PPy films were characterized using a scanning electron microscope (Hitachi S3000N) to study the surface morphology.

Electrochemical studies were carried out in a typical three-compartment cell connected to the CHI720c electrochemical workstation (CH Instrument Co., Austin, TX), using PPy- or CoPc/PPy-modified GC as the working electrodes, a platinum mesh as the counter electrode, and Ag/AgCl (3 M NaCl) as the reference electrode at room temperature. Before the measurements, the testing solution, 0.1 M $LiClO_4$/ACN–H_2O, was saturated with N_2 or CO_2.

The products that dissolved in the electrolyte were analyzed by high performance liquid chromatography (HPLC) (Shimadzu 20 A Series, Atlantis dC18 column using 20% ACN in Milli-Q water as a solvent) and used to determine the current efficiency.

Results and Discussion

Electrocatalytic CO_2 reduction at PPy electrode.— The cyclic voltammograms obtained using PPy as the working electrode in N_2- or CO_2-saturated electrolyte [0.1 M $LiClO_4$/ACN–H_2O (v:v = 10:1)] are presented in Fig. 1. They show a typical redox couple (labeled A/B) which could be attributed to the doping and dedoping of PPy in the N_2-saturated solution. When the solution was saturated with CO_2, a reduction peak due to the reduction of CO_2 was observed at −0.50 V. This is consistent with the results reported previously using polyaniline or PPy electrodes for CO_2 reduction under high pressure in methanol. In that work the catalytic effect was attributed to the adsorption of CO_2 via hydrogen-bond interactions with the polymer film.[22,23] The possible reaction pathways of CO_2 reduction at the PPy electrode could be described in the following manner

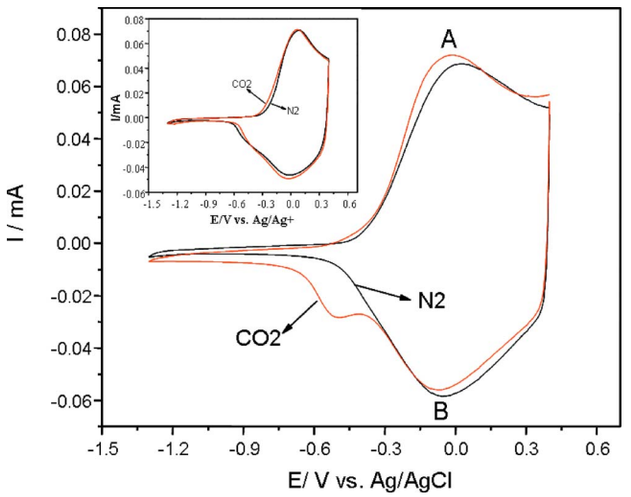

Figure 1. (Color online) CVs of the PPy electrode in 0.1 M $LiClO_4$/ACN–H_2O under N_2 and CO_2, υ = 50 mV/s (vs Ag/AgCl). The inset shows the CVs of the PPy electrode in the nonaqueous 0.1 M $LiClO_4$/ACN solution.

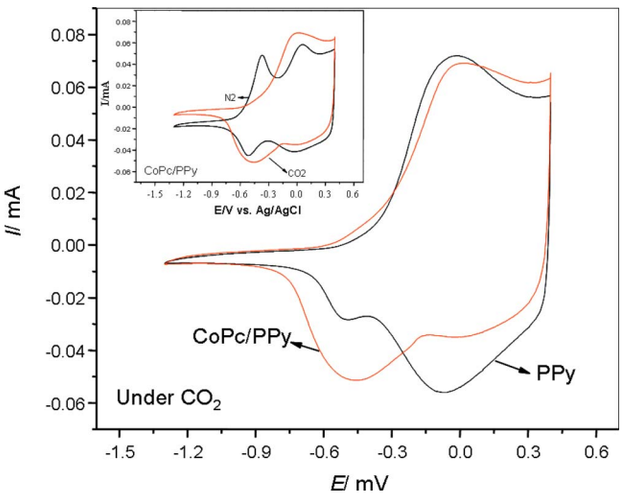

Figure 3. (Color online) CVs of PPy and Co/Pc/PPy electrodes in the CO_2-saturated electrolyte (vs Ag/AgCl). The inset shows CVs of the CoPc/PPy electrode in 0.1 M $LiClO_4$/ACN–H_2O under N_2 and CO_2, υ = 50 mV/s.

$$H^+ + e^- \rightarrow H_{ads}$$

$$CO_2 + H_{ads} \rightarrow HCOO_{ads}$$

$$HCOO_{ads} + H_{ads} \rightarrow HCOOH$$

The reaction is proposed to begin with the formation of H_{ads}, that is, the initial step is H_{ads} formation, then H_{ads} is added to CO_2 molecules, and $HCOO_{ads}$ is formed, which can recombine with further H_{ads} to give formic acid. This is one of the indirect ways in the electrochemical reduction of CO_2. The main role of the PPy film may be the adsorption of the substrate molecules via hydrogen bonding, so the transfer of a H_{ads} atom to the CO_2 molecule would be much easier and faster.

The inset of Fig. 1 shows the cyclic voltammograms obtained using the PPy-modified electrode in the nonaqueous 0.1 M $LiClO_4$/ACN electrolyte saturated with either N_2 or CO_2. No electrocatalytic CO_2 reduction was observed in the CO_2-saturated nonaqueous solution under identical conditions. This suggests that PPy has no catalytic effect for CO_2 reduction in the nonaqueous ACN solution, and the presence of H_2O is necessary and critical for the indirect reduction of CO_2. We assume that the reduction adsorption of H^+ arising from H_2O (10% in the mixed solvent) plays a key role in the subsequent catalyses of CO_2 reduction.

Electrocatalytic CO_2 reduction at CoPc/PPy electrode.— To improve the catalytic performance of PPy, the CoPc-modified PPy film was prepared by coating with the CoPc/THF material. The scanning electron microscopy (SEM) images of the PPy film with/without CoPc are shown in Fig. 2. The pure PPy displays a very smooth surface morphology (Fig. 2a), while the CoPc-modified PPy film (Fig. 2b) has a crystalline porous structure due to the CoPc coating.

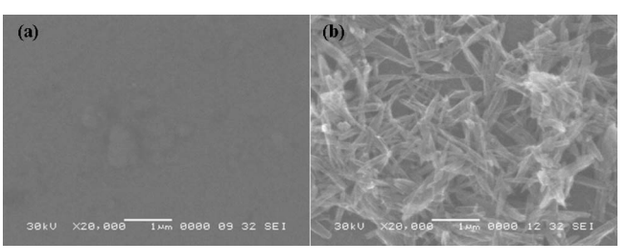

Figure 2. SEM image of (a) PPy and (b) CoPc/PPy electrodes.

After the preparation of the CoPc/PPy electrode, it was investigated for electrocatalytic CO_2 reduction under identical conditions used for the pure PPy electrode. The CVs using either PPy or CoPc/PPy as working electrodes were obtained in a CO_2-saturated 0.1 M electrolyte (Fig. 3). The electrocatalytic reduction of CO_2 took place at −0.18 V using the CoPc/PPy electrode, which showed a positive 160 mV shift in the onset of the reduction potential compared to that of pure PPy electrode (−0.34 V). This illustrates that the CoPc/PPy has a much better catalytic influence on CO_2 reduction than pure PPy. Furthermore, a higher catalytic peak current of CO_2 reduction is observed at −0.45 V using the CoPc/PPy electrode, which is probably caused by the increase in the number of active centers where the reduction of CO_2 takes place.[20,25]

Compared to the CV of the CoPc/PPy electrode in the N_2-saturated 0.1 M $LiClO_4$/ACN–H_2O solution, the inset of Fig. 3 shows that the oxidation peak of Co(I)Pc to Co(II)Pc disappeared in the presence of CO_2. The corresponding reduction peak of Co(II)Pc to Co(I)Pc under N_2 coincides less with that under CO_2 so that it is unclear whether the corresponding reduction peak is present in the CV under the CO_2 peak or not at all. The possible mechanism for this is that when H^+ is reduced to H_{ads} and H_{ads} is continuously consumed to reduce CO_2, it causes the oxidation of Co(I)Pc to Co(II)Pc.[20] It also suggests that a much stronger generation of H_{ads} occurred at the PPy and CoPc interfaces; therefore the CoPc/PPy composite electrode promoted the electrocatalytic reduction of CO_2 with enhanced catalytic activity compared to PPy alone.

Potentiostatic CO_2 reduction at PPy and CoPc/PPy electrodes.— CO_2 reduction was performed at a constant potential −0.8 V (vs Ag/AgCl) at both PPy and CoPc/PPy electrodes in the CO_2-saturated 0.1 M $LiClO_4$/ACN–H_2O (v:v = 1:1) solution. Figure 4 shows the *I-t* curve for catalytic CO_2 reduction at the CoPc/PPy electrode normalized from the pure PPy electrode with a stable current density of 20 mA/g. The higher catalytic current observed at the CoPc/PPy electrode again confirms that the PPy incorporated with CoPc has a better catalytic performance for CO_2 reduction than the PPy electrode itself (see inset of Fig. 4).

The product detected by HPLC was formic acid. No evolution of gaseous products was observed during the controlled potential electrolysis. This is consistent with the mechanism described in the first subsection for electrocatalyzed CO_2 reduction. This is possibly due

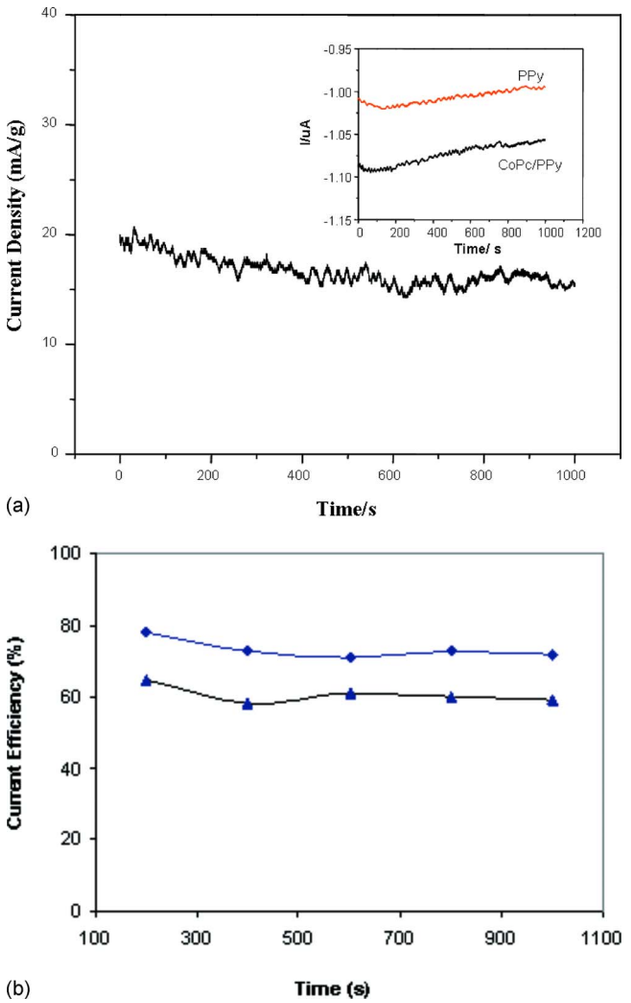

Figure 4. (Color online) (a) *I-t* curve for CO_2 reduction at the CoPc/PPy electrode normalized from the PPy electrode in 0.1 M $LiClO_4$/ACN–H_2O (vs Ag/AgCl). The inset is the *I-t* curve of the PPy- and CoPc/PPy-modified electrodes under CO_2. $E = -1.0$ V (vs Ag/AgCl). (b) Current efficiency–time diagrams of CO_2 reduction at PPy and CoPc/PPy electrodes.

to our use of the ACN-based solution without the addition of any other acid which is normally used in an aqueous environment. In the acidic aqueous solution, H^+ ions are used and involve the further proposed reaction pathways of CO_2 reduction in converting formic acid to acetic acid and formaldehyde. In this neutral organic environment, formic acid could not be oxidized to formaldehyde, which normally occurs in acid solution.[22] As the formic acid is the only major product detected under this situation, this simplifies the product separation process after CO_2 reduction. Based on the product analysis, Fig. 4b shows the calibrated current efficiency–time diagrams of electrocatalyzed CO_2 reduction at the CoPc/PPy electrode in 0.1 M $LiClO_4$/ACN–H_2O (v:v = 10:1). It indicates that for the CoPc/PPy electrode, the current efficiency tends to be constant at around 72%, which is higher than that (59%) of the PPy electrode. This suggests that less side reaction occurred using the CoPc/PPy electrode, which coincides with the improved catalytic performance.

Conclusion

The conversion of CO_2 into useful substances can be achieved using electrochemical methods. We have successfully prepared CoPc/PPy-modified GC electrodes and used them for the catalytic reduction of CO_2 in an ACN-based electrolyte. The reduction of CO_2 at the PPy electrode appears to involve the generation of H_{ads}, which could be significantly enhanced via coating the PPy film with CoPc. The onset potential of CO_2 reduction shifts to a more positive potential at the CoPc/PPy composite electrode from -0.34 (PPy) to -0.18 V. Furthermore, during potentiostatic electrolysis, the catalytic current for CO_2 reduction at CoPc/PPy was very stable with a higher current efficiency when compared to a single PPy electrode.

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